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CHEMOVISCOSEITY MODELING FOR THERMOSETTING RESINS - II

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ABSTRACT

A new analytical model for simulating chemoviscosity of thermosetting resin has been formulated. The model is developed by modifying the well-established Williams-Landel-Ferry (WLF) theory in polymer rheology for thermoplastic materials. By assuming a linear relationship between the glass transition temperature $T_g(t)$ and the degree of cure $\alpha(t)$ of the resin system under cure, the WLF theory can be modified to account for the factor of reaction time. Temperature-dependent functions of the modified WLF theory constants $C_1(T)$ and $C_2(T)$ were determined from the isothermal cure data of Lee, Loos, and Springer for the Hercules 3501-6 resin system. Theoretical predictions of the model for the resin under dynamic heating cure cycles were shown to compare favorably with the experimental data reported by Carpenter. This work represents progress toward establishing a chemoviscosity model which is capable of not only describing viscosity profiles accurately under various cure cycles, but also correlating viscosity data to the changes of physical properties associated with the structural transformations of the thermosetting resin systems during cure.

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FOREWORD

This work, performed at NASA - Langley Research Center (LaRC), was supported by the LaRC Polymeric Materials Branch (PMB) under Contract NAS1-18000. This is a progress report on an ongoing research project toward the chemoviscosity modeling for thermosetting resins, and is monitored by R. M. Baucom (PMB). Technical guidance provided by Dr. N. T. Wakelyn (PMB) and W. T. Freeman (PMB) with regard to the uses of LaRC IAF computing facilities and helpful discussions with Dr. J. A. Hinkley (PMB) during the course of this study are gratefully acknowledged.

CHEMOVISCOSITY MODELING FOR THERMOSETTING RESINS - II

I. INTRODUCTION

There are two different basic approaches in chemoviscosity modeling of thermosetting resin. One approach, typically represented by the work of Roller [1], is to empirically formulate a rate equation which relates the change of chemoviscosity with reaction time. For a resin system cured under a dynamic heating cure cycle (as commonly encountered in autoclave processing for composite materials), such an approach usually yields a model which is inadequate in describing accurately the nonlinearity of chemoviscosity as a function of reaction time. As Tajima and Crozier [2] pointed out, such a modeling approach renders itself to the limitation of batch-specific. The model parameters cannot be readily related to the chemical and rheological properties of the reacting system as well.

The second approach is based upon a modification to the well-established viscosity-temperature relationship existing in polymer rheology for thermoplastic materials. The parameters in such an equation can be expressed in terms of polymerization kinetics, and the chemoviscosity profiles as a function of reaction time can then be modeled for thermosetting resin systems.

The applicability of the modified Williams-Landel-Ferry (WLF) theory [3] in chemoviscosity modeling for thermosetting resin has been studied by Tajima and Crozier [2,4], Apicella et al. [5], and Hou [6] among others. It has been extensively documented in the literature that temperature-dependent viscosity of thermoplastic material can be accurately described by the WLF equations

within 100°K above its glass transition temperature (T_g). For a thermosetting resin system under cure, it is reasonable to assume that $T_g(t)$ of the material is always within 100°K lower than the cure temperature. The WLF equation should then be applicable to every instant state of the resin system under curing. The central theme in modifying the WLF theory to describe the chemoviscosity of thermosetting resin is to take into account the reaction time factor.

In an earlier paper [6], two assumptions were proposed, namely, that the rate constant of reaction, k_T , at any temperature T , is (i) diffusion controlled and is, therefore, inversely proportional to the viscosity $\eta_T(t)$ of the reactive medium, and (ii) directly proportional to the rate of change of glass transition temperature $T_g(t)$. The modified WLF equation becomes a first order ordinary nonlinear differential equation. Numerical solutions have also been shown to compare favorably with the experimental results for several thermosetting systems under isothermal and dynamic heating cure conditions. It has been concluded that the flexibility demonstrated by the modified WLF theory [6] can be conveniently exploited to establish an analytical model with high degree of accuracy for the chemoviscosity of any thermosetting resin system under various cure cycles. The physical significances of the material parameters selected for the model were, however, difficult to extract for the particular resin system under investigation.

As a next step toward the improvement of the chemoviscosity modeling for a thermosetting resin system, a new modification of the WLF theory is proposed in this report. Comparisons between the theoretical predictions and experimental data for chemoviscosity of a resin system (Hercules 3501-6) under both isothermal and dynamic heating cure conditions will be discussed.

List of Symbols

A_1, A_2, A_3	Material parameters (min^{-1}) specified in Table 1
a, b, c, d	Constants used in Eq. (5)
B	Material parameter specified in Table 1
$C_1(T), C_2(T)$	Temperature-dependent WLF constants defined by Eqs. (7) and (8)
DSC	Differential Scanning Calorimeter
$\Delta E_1, \Delta E_2, \Delta E_3$	Activation energies (J/mol) specified in Table 1
K_1, K_2, K_3	Material constants (min^{-1}) defined in Eqs. (3) and (4)
R	Universal gas constant ($=1.987 \text{ Cal/gm-mole/K}$)
T	Temperature ($^{\circ}\text{K}$)
T_c	Cure temperature ($^{\circ}\text{K}$), $T_c = T_g(\infty)$
$T_g(t)$	Glass transition temperature of the resin system under cure ($^{\circ}\text{K}$)
$T_g(\infty)$	Glass transition temperature of the resins system at completion of cure ($^{\circ}\text{K}$)
T_g^0	Glass transition temperature of the uncured resin system ($^{\circ}\text{K}$)
t	Cure time (minutes)
t_c	Time (minutes) defined in Eq. (6)
t_f	Time required for completion of cure (minutes)
Δt	Time interval (minutes) used in solving Eq. (9)
WLF	Williams-Landel-Ferry
$\eta_T(t)$	Chemoviscosity at temperature T (poises)
$\alpha(t)$	Degree of cure of the thermosetting resin during cure as determined by DSC thermal analysis

II. THEORY

The William-Landel-Ferry (WLF) theory [3] is given by

$$\log \left(\frac{\eta_T}{\eta_{T_g}} \right) = \frac{-C_1(T-T_g)}{C_2+T-T_g} \quad (1)$$

for $T_g < T < T_g + 100^\circ K$.

C_1 and C_2 are two material constants, and η_T represents viscosity at temperature T of the given thermoplastic material which possesses a glass transition temperature T_g . The normal use of the WLF equation for thermoplastic materials requires that T_g be constant while the temperature T is varied for the specific polymer under study. However, during cure of thermosetting resins, the monomers are initially polymerized and crosslinks are formed later. This is a system where $T_g(t)$ is changing and the curing temperature T is held constant (in an isothermal cure case, for example). The glass transition temperature T_g rises continuously and may eventually approach the curing temperature. Over the entire curing cycle, the material structure actually undergoes continuous phase transformations from a low molecular weight liquid to a high molecular weight polymeric melt, and eventually transforms to a crosslinked network. It is reasonable to assume that $T_g(t)$ of the material is always lower than the cure temperature T , and that $(T-T_g(t))$ is always within $100^\circ K$. The WLF theory (Eq. (1)) should then

be applicable to all of the different polymeric structure phases during cure. Before Eq. (1) can be applied to describe the chemoviscosity of the curing resin, however, modifications need to be made in order that reaction time, t , of the thermosetting resin system is properly taken into account. This can be accomplished as follows:

A simple assumption that $T_g(t)$ is a linear function of the degree of cure $\alpha(t)$ of the thermosetting resin can be made, which gives:

$$T_g(t) = T_g^0 + (T_c - T_g^0) \alpha(t) \quad (2)$$

where $T_g^0 = T_g(0)$ is the glass transition temperature of the unreacted resin system, T_c is the cure temperature in °K, and t is the reaction time in minutes. Equation (2) should satisfy the boundary conditions, namely,

$$T_g = T_g^0, \alpha = 0 \text{ at } t = 0$$

and

$$T_g = T_c, \alpha = 1 \text{ at } t = t_f$$

where t_f is the time required for completion of cure. The degree of cure $\alpha(t)$ for the resin system can be determined by means of thermal analysis. It is assumed that the degree of cure at time t is equal to the fraction of heat released as measured by a DSC up to time t for the thermosetting material under cure. The total heat of reaction can be determined for the experiments using dynamic temperature scanning. The degree of cure $\alpha(t)$ can then be

determined for different isothermal cure conditions [7,8]. The α 's thus determined are functions of curing temperature and time.

Equations (1) and (2) constitute a modified WLF theory for simulating chemoviscosity of thermosetting resin. Among the five material parameters, C_1 and C_2 can be determined as a function of temperature T by fitting with isothermal cure $n(\alpha)$ data, $n_{T_g} = 10^{13}$ poises is given by Gordon and Simpson [9] for many polymeric materials at $T = T_g$, and T_g^0 can be determined by DSC thermal analysis. In an isothermal cure case, T_c of Eq. (2) is equal to cure temperature. In the dynamic heating case, however, T_c is difficult to specify exactly and is the only adjustable variable in the present modified WLF theory.

III. EXPERIMENTAL DATA

For the purpose of evaluating model predictions of this modified WLF theory, experimental data on Hercules 3501-6 epoxy resin reported in the literature by Lee, Loos, and Springer [8] and Carpenter [10] were selected. These data will be summarized briefly.

Degree of Cure $\alpha(t,T)$

Lee et al. [8] performed thermal analyses on the epoxy resin system using a Differential Scanning Calorimeter (DSC). The degree of cure α and the rate of degree of cure $d\alpha/dt$ were determined from the results of the isothermal scanning experiments. Eight different temperatures were selected, and the results are reproduced in Figure 1. It is noted from the figure that both higher values of the degree of cure and rate of degree of cure can be obtained at higher cure temperatures. The rate of degree of cure is a decreasing function of cure time t , and eventually levels off at a low rate value (< 0.1) when a high degree of cure is reached. The following equations were found to describe these temperature-dependent data accurately:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha) (1-\alpha) (B-\alpha) \quad \text{for } \alpha \leq 0.3 \quad (3)$$

$$\frac{d\alpha}{dt} = K_3 (1-\alpha) \quad \text{for } \alpha > 0.3 \quad (4)$$

where

$$K_1 = A_1 \exp (-\Delta E_1/RT)$$

$$K_2 = A_2 \exp (-\Delta E_2/RT)$$

$$K_3 = A_3 \exp (-\Delta E_3/RT)$$

Values of constants in Eqs. (3) and (4) are shown in the Table below.

Comparisons between the measured values of $d\alpha/dt$ and the values calculated by Eqs. (3) and (4) are also shown in Figure 1.

Table 1. The values of the constants of Eqs. (3) and (4)
for Hercules 3501-6 Resin System [8]

$$B = 0.47$$

$$A_1 = 2.101 \times 10^9 \text{ min}^{-1}$$

$$A_2 = -2.014 \times 10^9 \text{ min}^{-1}$$

$$A_3 = 1.960 \times 10^5 \text{ min}^{-1}$$

$$\Delta E_1 = 8.07 \times 10^4 \text{ J/mol}$$

$$\Delta E_2 = 7.78 \times 10^4 \text{ J/mol}$$

$$\Delta E_3 = 5.66 \times 10^4 \text{ J/mol}$$

Eqs. (3) and (4) can be integrated provided that the temperature is kept constant. The following relationships between α and t are obtained:

$$t = \frac{a}{K_2} \ln \left(1 + \frac{K_2}{K_1} \alpha \right) - b \ln (1-\alpha) - c \ln \left(1 - \frac{\alpha}{B} \right) \quad (5)$$

$$t = -\frac{1}{K_3} \ln \left(\frac{1-\alpha}{0.7} \right) + t_c \quad (6)$$

where

$$\begin{aligned}a &= K_2^2 (B-1)/d \\b &= - (K_1 + K_2)/d \\c &= (K_1 + K_2 B)/d \\d &= (K_1 + K_2) [K_1 B^2 + (K_1 - K_2) B - K_1]\end{aligned}$$

and t_c is the time given by Equation (5) for $\alpha = 0.3$.

Chemoviscosity $\eta(t,T)$

Chemoviscosity of the resin under an isothermal cure condition were measured by Lee et. al. [8] on a Rheometrics parallel disc and plate mechanical spectrometer Model 605. The radius of the disc was 25 mm and the gap between the disc and the plate was 0.5 mm. A frequency of 1.6 Hz was employed. For a given cure temperature, the $\eta(t)$ measured can be related to $\alpha(t)$ obtained from DSC thermal analysis. The results are plotted in Figure 2 for three different isothermal cure cases. It is again noted that at a higher cure temperature, higher values of the degree of cure can be reached. For a given α , the decrease in viscosity is attributed to the temperature effects.

Chemoviscosities of the 3501-6 epoxy resin cured under dynamic heating conditions were reported by Carpenter [10]. Carpenter measured chemoviscosities at different rate of increase in temperatures and reported the measured values as a function of cure time. The experimental data shown here are for resins cured at constant heating rates of 1°K/min (figure 5), 2.17 and 5°K/min (Figure 6) and a cure cycle (Figure 8) similar to the one typically found in autoclave processes for composite materials.

The procedure used for model evaluations will be as follows:

1. Model parameters of Eqs. (1) and (2) will be determined first by the experimental data of Lee et al. [8] under isothermal cure conditions. Temperature-dependent material constants $C_1(T)$ and $C_2(T)$ can thus be determined.
2. The chemoviscosity model $\eta(t,T)$ established by isothermal cure data under procedure 1 will then be made to follow various dynamic heating cure cycles $T(t)$. The viscosity values thus calculated will be compared with the experimental data reported by Carpenter [10].

IV. MODEL PREDICTIONS AND DISCUSSION

Isothermal case

Gordon and Simpson [9] pointed out that glass-forming substances generally have the same shear viscosity of $\eta_{T_g} = 10^{13}$ poises at their T_g , and this has also been confirmed for polymer systems. By specifying $T^0 = 300^\circ\text{K}$ (27°C) in Eq. (2), the model (i.e., Eqs. (1) and (2)) can then be fitted to the experimental data $\eta(\alpha)$ as shown in Figure 2 provided that proper values of material constants C_1 and C_2 are selected. C_1 and C_2 determined for different temperatures are tabulated below, and the model predictions are drawn as solid lines in the figure.

Table 2. Values of material constants C_1 and C_2 in the modified WLF Theory for Hercules 3501-6 resin system as determined by the isothermal cure data.

T_c ($^\circ\text{K}$)	C_1	C_2 ($^\circ\text{K}$)
375	21.1	53.0
400	17.1	33.6
425	18.5	46.0

The model is capable of describing the nonlinear relationship between viscosity, η , and the degree of cure, α , as shown in Figure 2, especially for

the case of higher cure temperature. This is considered a significant improvement over the empirical linear model used by Lee, Loos, and Springer [8]. An arrhenius type of plot is arbitrarily chosen for C_1 and C_2 as shown in Figure 3. The data is rather scattered. Due to the (unfortunate) limitation on size of the experimental data and the wide range in temperatures covered by the dynamic heating cure experiments (as will be discussed later), a linear least squares fit was chosen. The straight lines are represented, respectively, by:

$$\log C_1 = 186.02 (1/T) + 0.8084 \quad (7)$$

and

$$\log C_2 = 212.16 (1/T) + 1.106 \quad (8)$$

It is noted that in the analysis described above, the glass transition temperatures $T_g(t)$ for the varying molecular structures of the resin cured at different temperatures are chosen as reference temperatures. C_1 and C_2 are therefore treated as "universal constants" in the present context. Values of C_1 and C_2 reported in Table 2 are close to the values of 17.44 and 51.6, respectively, once reported by Williams et al. [3] as the universal constants for all polymeric materials systems. Eqs. (7) and (8) will still be used, however, to account for temperature-dependences of C_1 and C_2 in chemoviscosity simulation under dynamic heating cure conditions.

The theoretical assumptions as described above, which yield close values for the WLF constants C_1 and C_2 , respectively, among three different

isothermal curing temperatures, are also supported by the parallelism among experimental data observed in Figure 2 for $\alpha < 0.3$. Data of higher values of both n and α are difficult to be measured, and could be considered less accurate.

Dynamic Heating Case

In the case of dynamic heating cure conditions, integrations of Eqs. (3) and (4) are very difficult to perform. If one assumes that within any time interval $\Delta t = t_2 - t_1$, the temperature T_C is uniform, and is equal to $(T_1 + T_2)/2$, where T_1 and T_2 are temperatures at t_1 and t_2 respectively as defined by the cure cycle, Eqs. (3) and (4) become:

$$\begin{aligned} \Delta t &= t_2 - t_1 \\ &= f(\alpha_2, T_C) - f(\alpha_1, T_C) \end{aligned} \quad (9)$$

where

$$f(\alpha, T_C) = \frac{a}{K_2} \ln \left(1 + \frac{K_2}{K_1} \alpha \right) - b \ln(1 - \alpha) - c \ln \left(1 - \frac{\alpha}{B} \right), \text{ for } \alpha \leq 0.3$$

and

$$f(\alpha, T_C) = -\frac{1}{K_3} \ln \left(\frac{1 - \alpha}{0.7} \right) + t_C \quad \text{for } \alpha > 0.3$$

The parameters a , b , c , and t_c are the same as defined before in Eqs. (5) and (6). The value of the increased degree of cure α_2 in Eq. (9) can be calculated by the Generalized Newton's Method. Details of the solution schemes are summarized in the Appendix.

Values of $\alpha(t)$ determined by the scheme described above depend heavily on the time interval Δt chosen. Theoretically more accurate $\alpha(t)$ can be determined numerically when a smaller Δt is used. On the other hand, a smaller Δt could increase dramatically the numerical round-off errors. A series of Δt values were selected, and $\alpha(t)$ was calculated from Eq. (9) for a cure cycle with a constant heating rate of $5^\circ\text{K}/\text{min}$. The results are plotted in Figure 4. It can be seen that numerical round-off errors become dominant when $\Delta t < 0.05 \text{ min}$. It is also noted that numerical values of $\alpha(t)$ calculated for $\Delta t = 0.5$ and 1.0 minute , respectively, are almost indistinguishable. Consequently, $\Delta t = 0.5 \text{ minute}$ was chosen for all calculations discussed below.

Chemoviscosities of the Hercules 3501-6 epoxy resin system under dynamic heating cure conditions were reported by Carpenter [10]. Data for these constant rates of heating experiments are reproduced in Figures 5 and 6. The heating rates are 1.0 , 2.17 , and $5^\circ\text{K}/\text{min}$ respectively. All cure cycles started from 300°K (27°C). Temperature-dependent $C_1(T)$ and $C_2(T)$ as defined by Eqs. (7) and (8) are followed in the simulation. Values of the rest of the parameters used in the model are tabulated below:

Table 3. Values of model parameters used in simulating chemoviscosity under rate of heating cure conditions

Heating rate (°K/min)	η_{T_g} (poises)	T_g^0 (°K)	T_c (°K)
1	10^{13}	300	415
2.17	10^{13}	300	430
5	10^{13}	300	450

The model predictions are shown as solid curves in Figures 5 and 6. It is noted that the theoretical calculations compared favorably with the experimental data for all three cases.

Theoretically, T_c is equal to $T_g(\alpha)$ at $T \rightarrow \infty$ or $\alpha \rightarrow 1$ (see Eq. (2)). Under the dynamic heating cure conditions, however, T_c is difficult to specify. Values of T_c (in Table 3) in the above calculations were selected arbitrarily such that model predictions are in reasonably good agreement with the experimental data. Nevertheless, higher values of T_c (Table 3) resulting from the simulation of higher rates of heating experiments, are in agreement with physical observations for thermosetting resins.

The calculated degree of cure $\alpha(t)$ for all three cases is plotted in Figure 7. These calculated $\alpha(t)$ are based on the experimental data for the resin under isothermal cure conditions [8], and are independent of the arbitrarily selected values of T_c discussed above. Values of $d\alpha/dt$ go

through maxima for all three cases. The arrow marks shown in the figure denote the times when chemoviscosities approach infinity during cure. These arrow marks are located approximately at $\alpha(t) = 0.75 \pm 0.05$, and are near the inflection points of the curves as well. Physical significances of these observations are unclear at the present time, and further research in the future is required.

Chemoviscosity was also measured by Carpenter [10] for the 3501-6 resin system under a typical cure cycle used in autoclave processing for composite materials. The experimental data is reproduced in Figure 8. Values of model parameters used are the same as those included in Table 3 and Eqs. (7) and (8), except that $T_C = 375^\circ\text{K}$. The theoretical predictions, shown as solid curves, are seen in reasonably good agreement with the experimental data. The model, however, fails to describe the chemoviscosity "shoot-up" near the end of the cure cycle. The reasons are unclear at the present time. It could be due to the inadequate definitions of $C_1(T)$ and $C_2(T)$ by Eqs. (7) and (8); or due to different reaction mechanisms appeared in the high curing temperature regime. Calculated values of $\alpha(t)$ are plotted in Figure 9. The arrow mark shown denotes the time when chemoviscosity "shoot-up" occurs. Features of the $\alpha(t)$ curve discussed above for isothermal cure cases are again noticeable in this figure.

Temperature ranges covered by Carpenter [10] in dynamic heating cure experiments, as shown by dotted lines in Figure 3, far exceed the ranges covered by Lee et al. [8] in isothermal cure experiments (shown by solid lines in the figure). Accurate definitions of the crucial temperature-dependences of $C_1(T)$ and $C_2(T)$ needed for the model thus suffer from serious data

extrapolation errors. The results of the present investigations, although encouraging, can only demonstrate the feasibility of the approach of modifying the WLF theory in chemoviscosity modeling for thermosetting resin. Detailed studies such as the precise definitions of $T_g(\alpha)$ (Eq. (2)), and the functions of $C_1(T)$ and $C_2(T)$ over the full temperature range by experimental measurements for the resin system under investigation have to be pursued in the future.

V. CONCLUSIONS

A new analytical model, based upon modifications of the WLF theory, has been formulated. The model assumes that the glass transition temperature $T_g(t)$ of the resin system under cure is linearly related to the degree of cure $\alpha(t)$ determined by DSC thermal analysis. Theoretical predictions of the chemoviscosity compare favorably with the experimental data reported in the literature for both isothermal and dynamic heating cure conditions. Considering that data are available only in the relatively narrow temperature range used in isothermal curing experiments by Lee, Loos, and Springer [8], the agreement between theoretical predictions and experimental data reported by Carpenter [10] for dynamic heating cure cycles are particularly encouraging. Due to the limitations in size of the data available, the successful analysis reported here has established the feasibility of the proposed approach which simulates chemoviscosity for thermosetting resin by modifying the widely used WLF theory in polymer rheology.

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Appendix - Generalized Newton's Method in Solving α_2 from Eq. (9)

Eq. (9) can be rearranged to become:

$$g(\alpha_2) = f(\alpha_2, T_C) - f(\alpha_1, T_C) - \Delta t_C = 0 \quad (a)$$

and

$$g'(\alpha_2) = f'(\alpha_2, T_C) \quad (b)$$

where $g'(\alpha_2) = dg/d\alpha_2$, and $f'(\alpha_2, T_C) = df/d\alpha_2$. The Generalized Newton's Method sets up the following recursion formula to solve for α_2 in Eq. (a):

$$\alpha_2^{n+1} = \alpha_2^n - w \cdot g(\alpha_2^n)/g'(\alpha_2^n), \quad n = 0, 1, 2, \dots \quad (c)$$

provided that $g'(\alpha_2) \neq 0$; where w is called the over-relaxation factor. A good choice for w can be determined, in general, only by experimentation. A choice of w different from unity often can increase the convergence rate of the routine appreciably. In this study, $w = 0.1$ was used for all calculations. Iterations are continued until $|\alpha_2^{n+1} - \alpha_2^n| \leq 10^{-6}$.

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- Figure 1. Rate of degree of cure vs. degree of cure reported by Lee, Loos, and Springer [8] for Hercules 3501-6 resin system under isothermal cure cycles. Solid lines were calculated using Eqs. (3) and (4).
- Figure 2. Chemoviscosity as a function of degree of cure for Hercules 3501-6 resin system under isothermal cure cycles. Symbols represent experimental data reported by Lee, Loos, and Springer [8]. Solid lines were calculated by the model, Eqs. (1) and (2).
- Figure 3. Temperature-dependences of the WLF constants C_1 and C_2 determined by the isothermal cure data of Lee et al. [8] for the Hercules 3501-6 resin system.
- Figure 4. Simulated degree of cure data for the Hercules 3501-6 resin system cured under constant rate of heating condition, $5^{\circ}\text{K}/\text{min}$. Various time intervals Δt were used in solving Eq. (9).
- Figure 5. Chemoviscosity of the Hercules 3501-6 resin system cured under constant rate of heating condition of $1^{\circ}\text{K}/\text{min}$. Circles denote experimental data by Carpenter [9]. Solid curve denotes the model predictions of Eqs. (1) and (2).
- Figure 6. Chemoviscosity of the Hercules 3501-6 resin system cured under constant rates of heating conditions of 2.17 and $5^{\circ}\text{K}/\text{min}$, respectively. Circles denote the experimental data by Carpenter [9]. Solid curves denote the model predictions of Eqs. (1) and (2).
- Figure 7. Simulated degree of cure for the Hercules 3501-6 resin system cured under constant rate of heating conditions indicated.
- Figure 8. Chemoviscosity of the Hercules 3501-6 resin system cured under the cure cycle shown. Circles denote the experimental data by Carpenter [9]. Solid curve was calculated by the model, Eqs. (1) and (2).
- Figure 9. Simulated degree of cure data for the Hercules 3501-6 resin system cured under the cure cycle included.

Composite Processing Laboratory Research Reports

Polymeric Materials Branch, Langley Research Center
National Aeronautics and Space Administration

- CPL 1.** "A Theoretical Study of Resin Flows for Thermosetting Materials During Prepreg Processing," NASA CR-172442, July, 1984, by T. H. Hou (Kentron).
- CPL 2.** "Chemoviscosity Modeling for Thermosetting Resins - I," NASA CR-172443, November, 1984, by T. H. Hou (Kentron).
- CPL 3.** "Correlation of Dynamic Dielectric Measurements with Viscosity in Polymeric Resin Systems," 30th National SAMPE Symposium and Exhibition, Anaheim, CA., March, 1985, pp 638-648, by D. Kranbuehl, S. Delos, E. Yi, J. Mayer (W&M), T. H. Hou (Kentron), and W. P. Winfree (LaRC).
- CPL 4.** "On the Applications of WLF Theory to Thermosetting Resins," SPE ANTEC, Washington, D.C., April, 1985, pp 1253-1255, by T. H. Hou (Kentron).
- CPL 5.** "Chemoviscosity Modeling for Thermosetting Resins - II," NASA CR-177958, August, 1985, by T. H. Hou (PRC Kentron, Inc.)

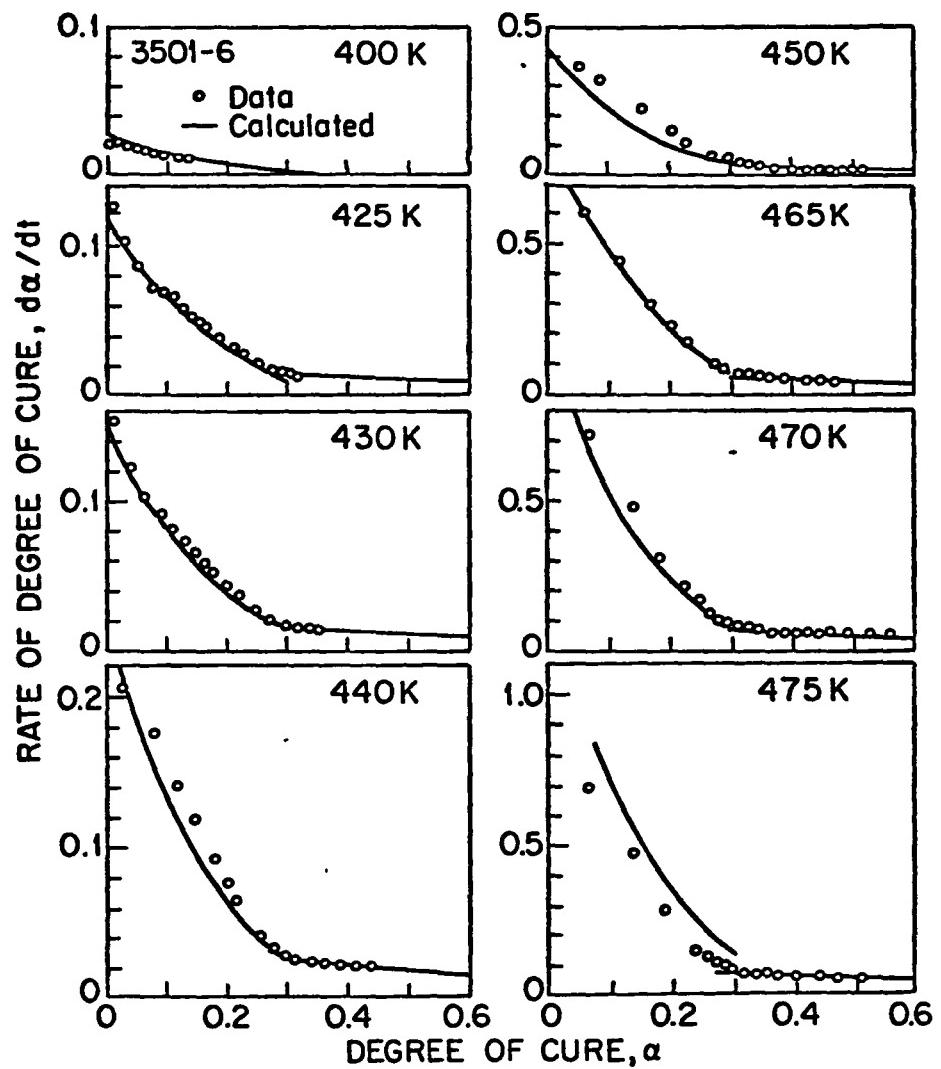


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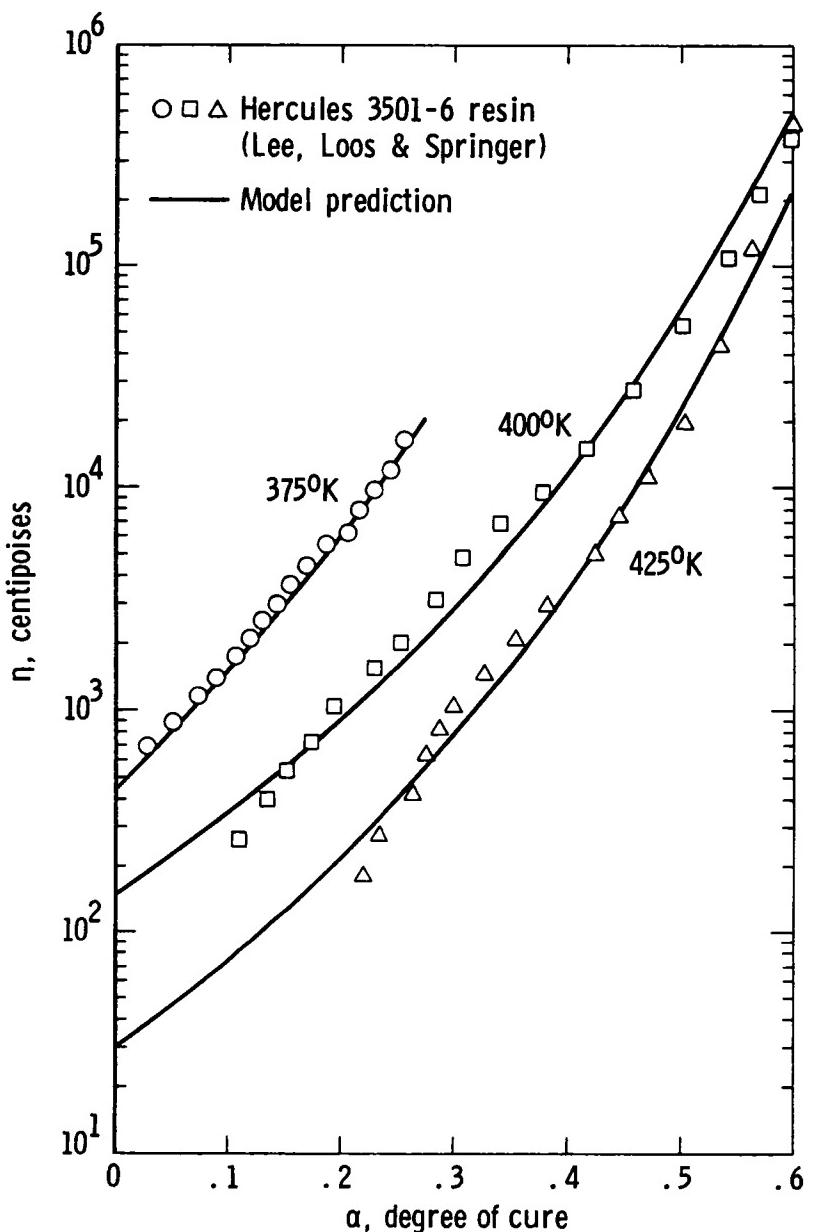


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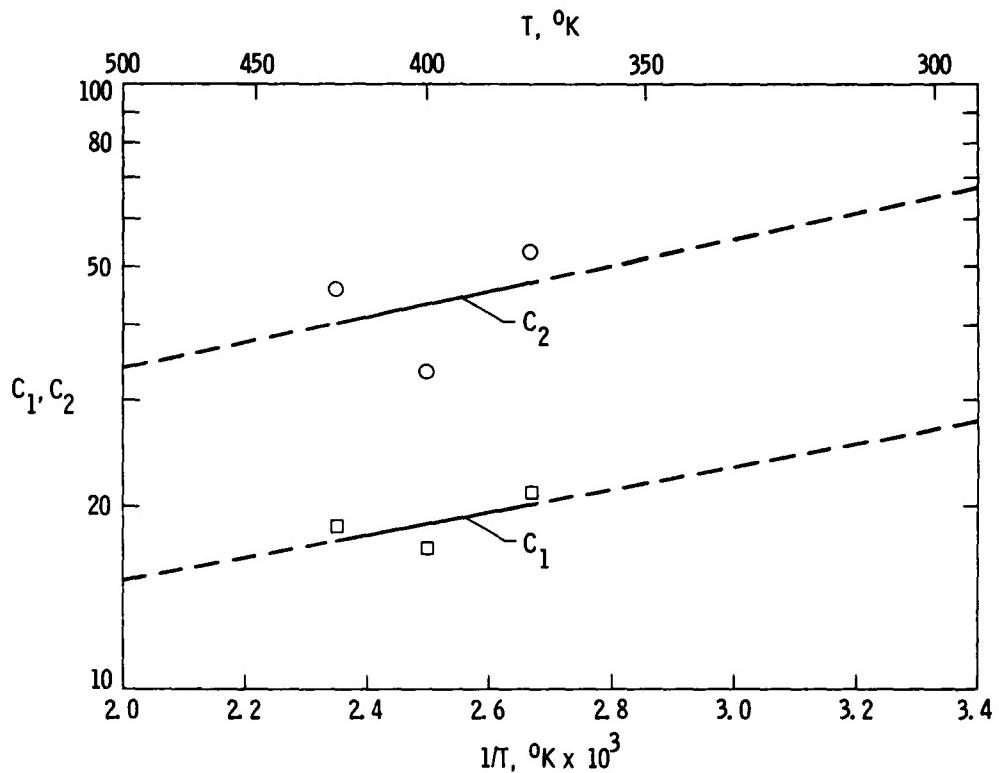


Figure 3. Temperature-dependences of the WLF constants C_1 and C_2 determined by the isothermal cure data of Lee et al. [8] for the Hercules 3501-6 resin system.

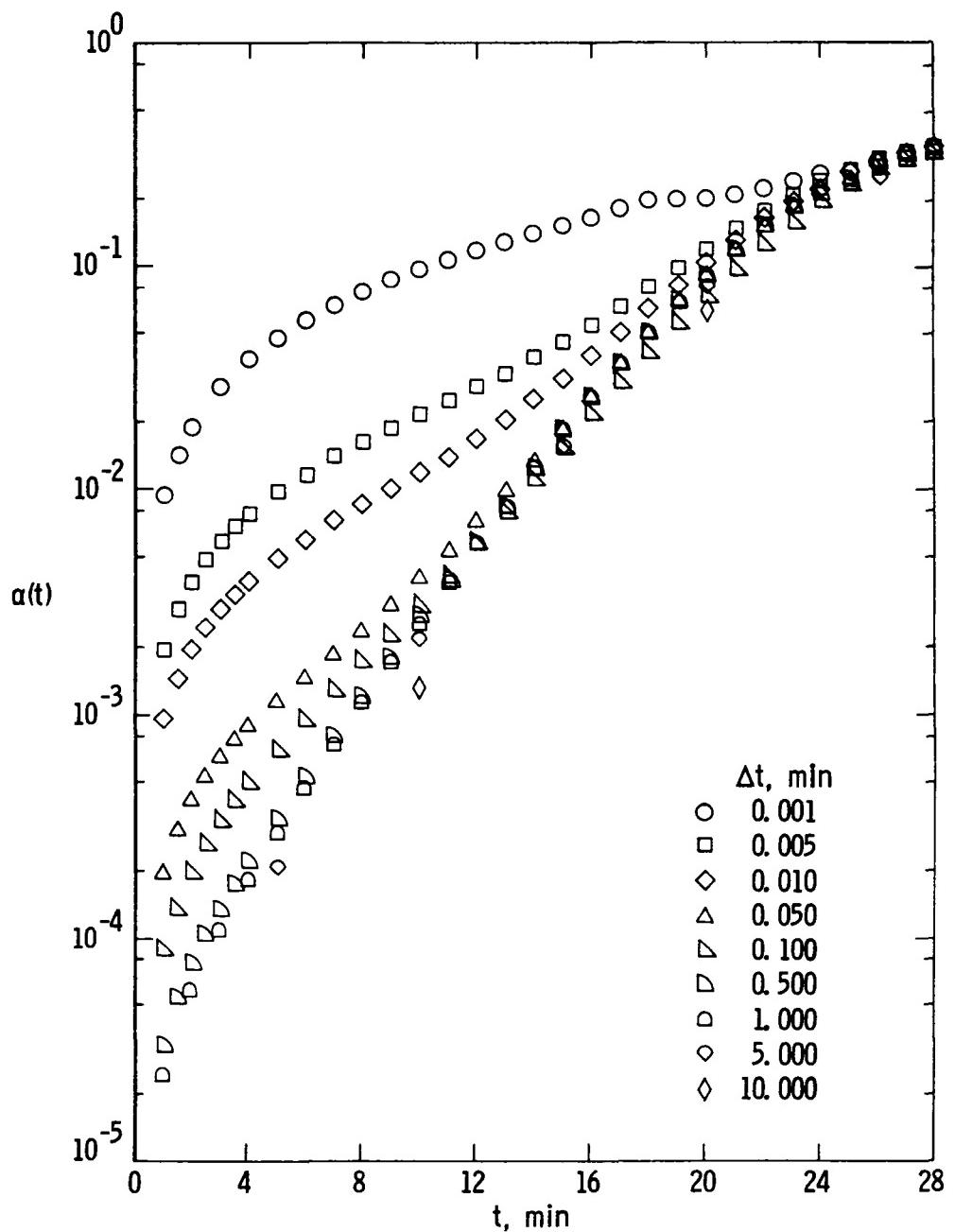


Figure 4. Simulated degree of cure data for the Hercules 3501-6 resin system cured under constant rate of heating condition, $5^{\circ}\text{K}/\text{min}$. Various time intervals Δt were used in solving Eq. (9).

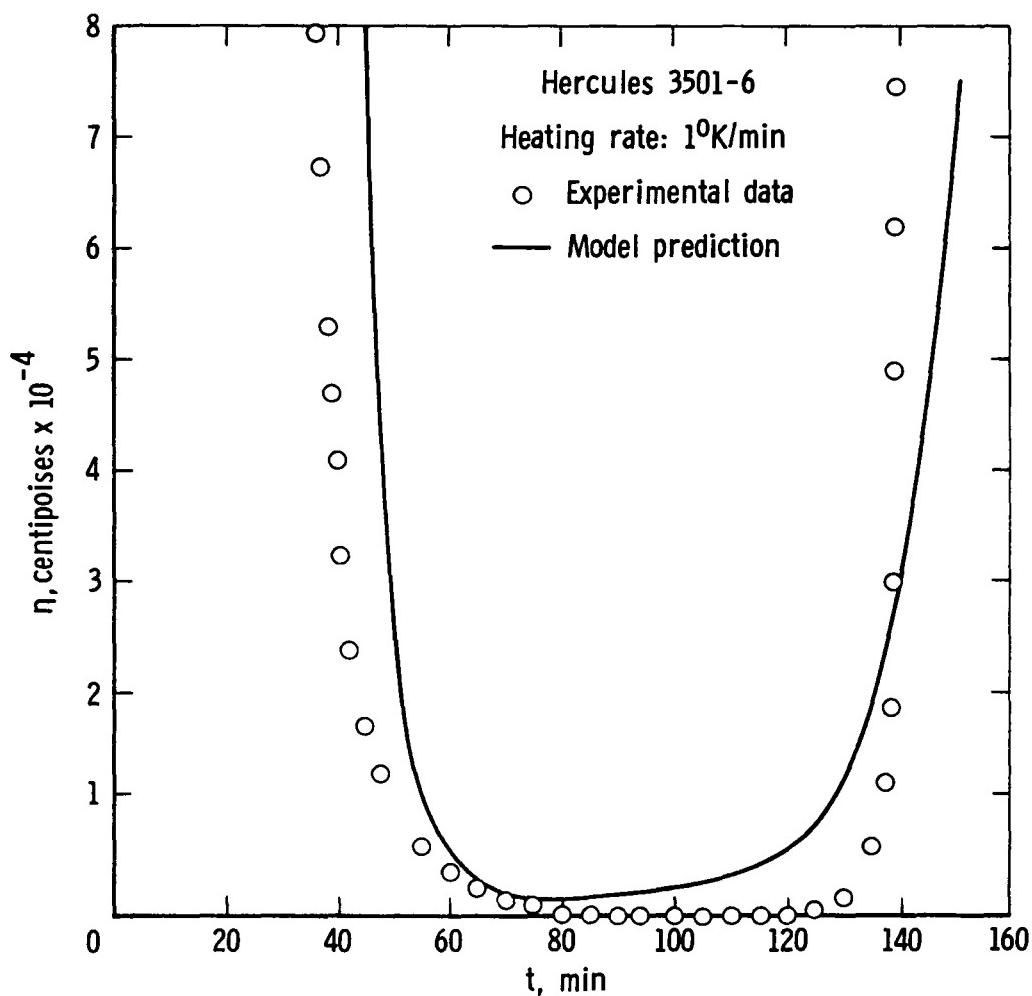


Figure 5. Chemoviscosity of the Hercules 3501-6 resin system cured under constant rate of heating condition of 1°K/min. Circles denote experimental data by Carpenter [10]. Solid curve denotes the model predictions of Eqs. (1) and (2).

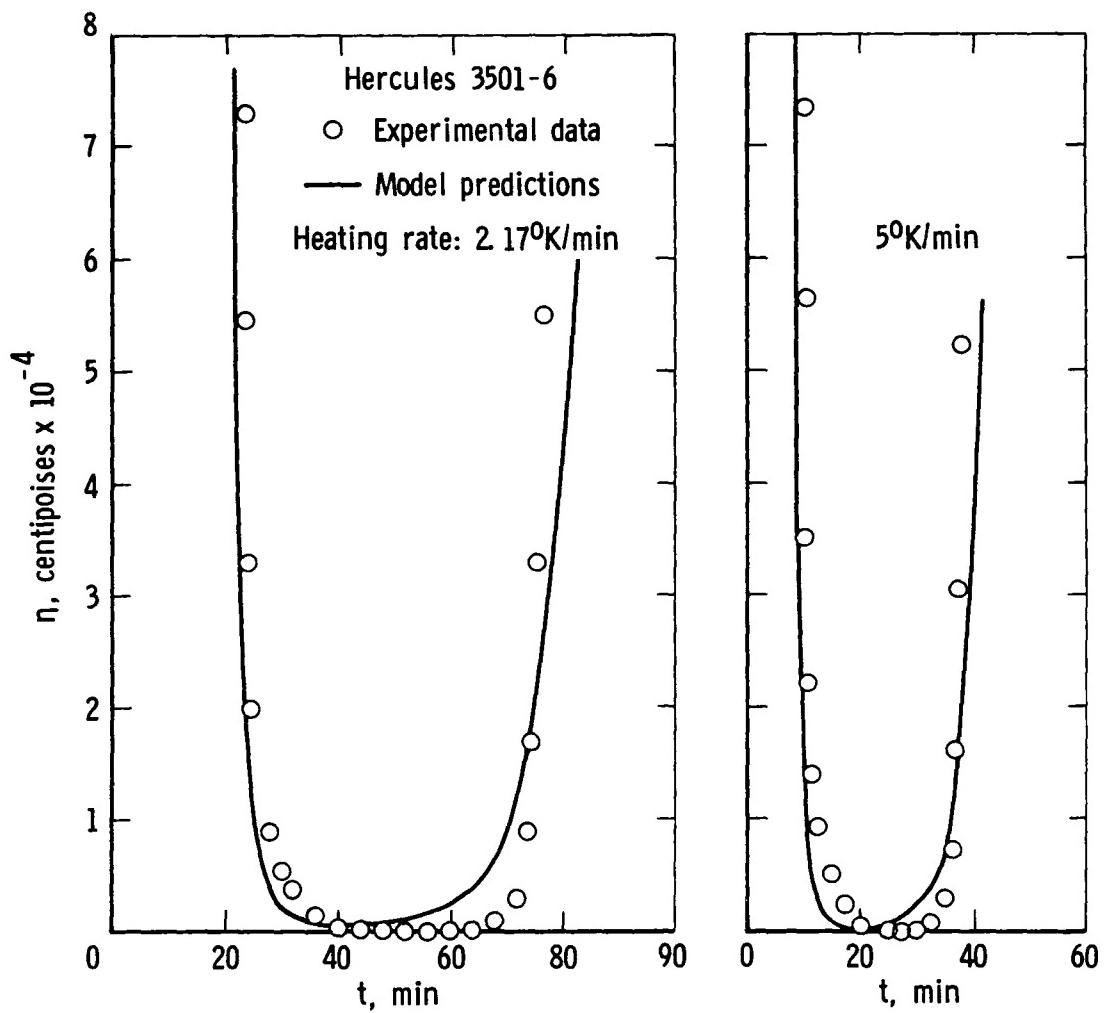


Figure 6. Chemoviscosity of the Hercules 3501-6 resin system cured under constant rates of heating conditions of 2.17 and 5°K/min, respectively. Circles denote the experimental data by Carpenter [10]. Solid curves denote the model predictions of Eqs. (1) and (2).

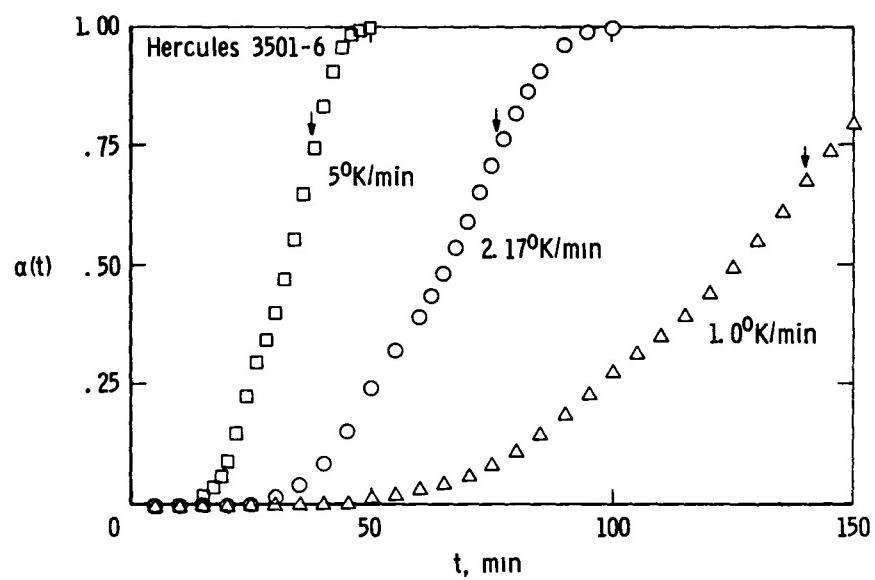


Figure 7. Simulated degree of cure for the Hercules 3501-6 resin system cured under constant rate of heating conditions indicated.

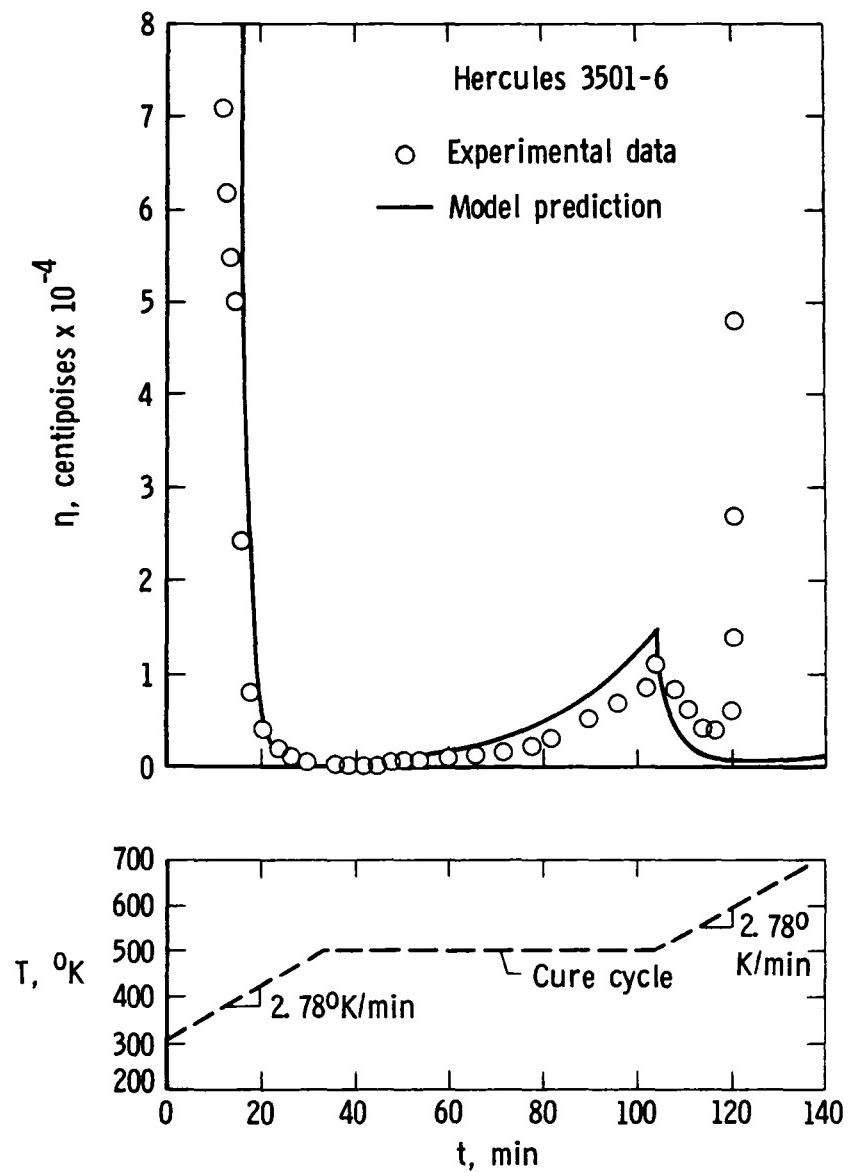


Figure 8. Chemoviscosity of the Hercules 3501-6 resin system cured under the cure cycle shown. Circles denote the experimental data by Carpenter [10]. Solid curve was calculated by the model, Eqs. (1) and (2).

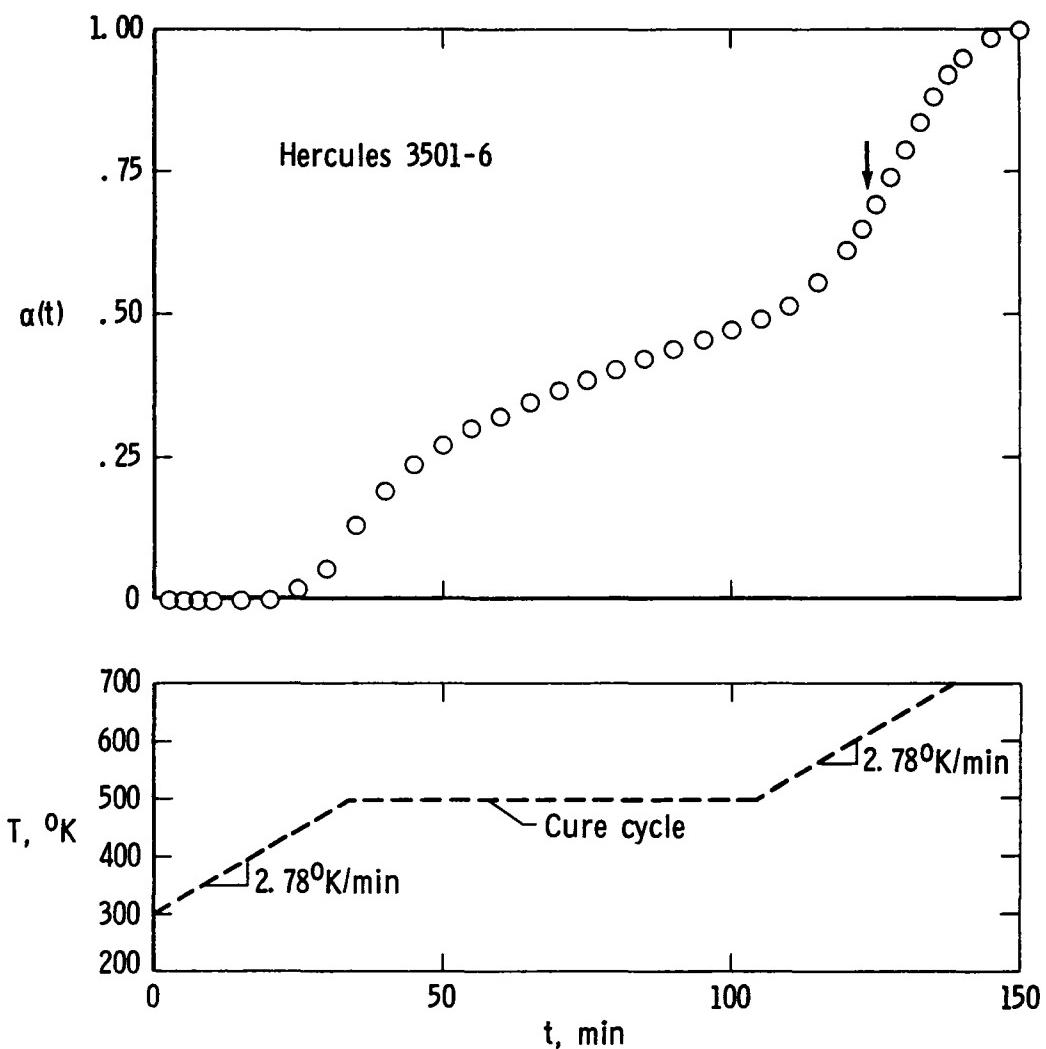


Figure 9. Simulated degree of cure data for the Hercules 3501-6 resin system cured under the cure cycle included.

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